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OPTIMIZATION OF CERAMIC GRANITE COMPOSITIONS

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The composition of ceramic granite, which is a new kind of facing ceramics, is upgraded. Regularities in the variation of the properties of experimental mixtures in relastion to the content of their main components are established. The content of quartz and feldspar in the granite mixture compositions is optimized, and the effect of the temperature on their sintering is studied.

For a long time facing ceramics produced by single-stage firing have been regarded as a material with good technical properties (strength, wear resistance, density, waterproofness); however, its aesthetic qualities have left much to be desired. Glazing of such products involves a number of technological problems and is not always efficient.

The situation changed with the appearance on the market of a new variety of facing ceramics, namely, ceramic granite ("gres"). Synthetic granite can be classified as a sintered product with a porcelain-like structure. It has high physicomechanical parameters and good decorative properties. This is achieved, for instance, by mixing differently tinted ceramic powders, and a combination of 3 – 4 colors makes it possible to obtain interesting chromatic effects. Among the known materials are "macrogranites" produced on the basis of granulated powders whose texture is formed by a combination of granules of different tints and sizes (from 0.1 to 5 mm). Some granites are tinted by soluble salts, which makes it possible to obtain irregular diffuse color contours with gradual transitions to each other. In this way the structure of natural marble, gabbro, etc. is reproduced.

The technology of ceramic granite production is similar to the technology of production of floor files. In particular, preference is given to the moist method of mixture preparation. Fine milling increases the reactivity of the stony mixture components, which are relatively inert at normal temperature, by providing destruction of their structure and partial deformation of the crystal lattice. A special feature of the granite production technology is fast single-stage firing (more than 2000 K/h), which imposes high requirements on the crack resistance and deformation resistance of the ceramic mixtures used in the process.

The main raw material components in granite production are: high-quality white-burning clays, which impart cohesion and mechanical strength to the material and provide its sinterability in firing; kaolin, which serves to increase the crock whiteness; feldspar or pegmatite, which decreases the sintering temperature; quartz material to improve the mechanical strength and control the TCLE of material. Mixture compositions and production technology are described in the literature [1]. Production practice, however, indicates that certain difficulties arise in the production of "gres" tiles that are related to substitution of raw materials and the influence of the mineralogical composition of the materials; furthermore, the reasons for the tendency for product cracking under machine treatment (grinding) are not fully clarified; and the problem of contamination of the product surface in service is not solved.

That is why the problem of optimization of mixture compositions for granite production and investigation of the effect of their chemical and mineralogical composition on the processes of phase and structure formation in the crock, which are the main subjects of the present study, remain topical.

The raw materials used in the study were Keramik-Vesko clay, Glukhovetskoe kaolin, and Loevskoe quartz sand.

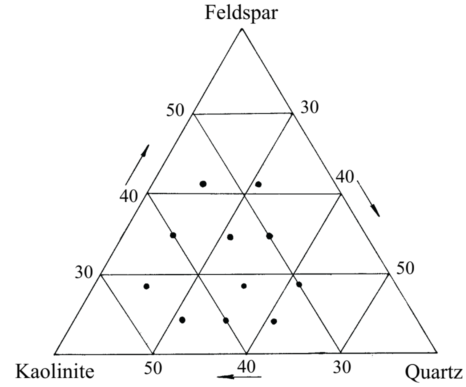

Fig. 1. Region of experimental compositions in the ternary system.

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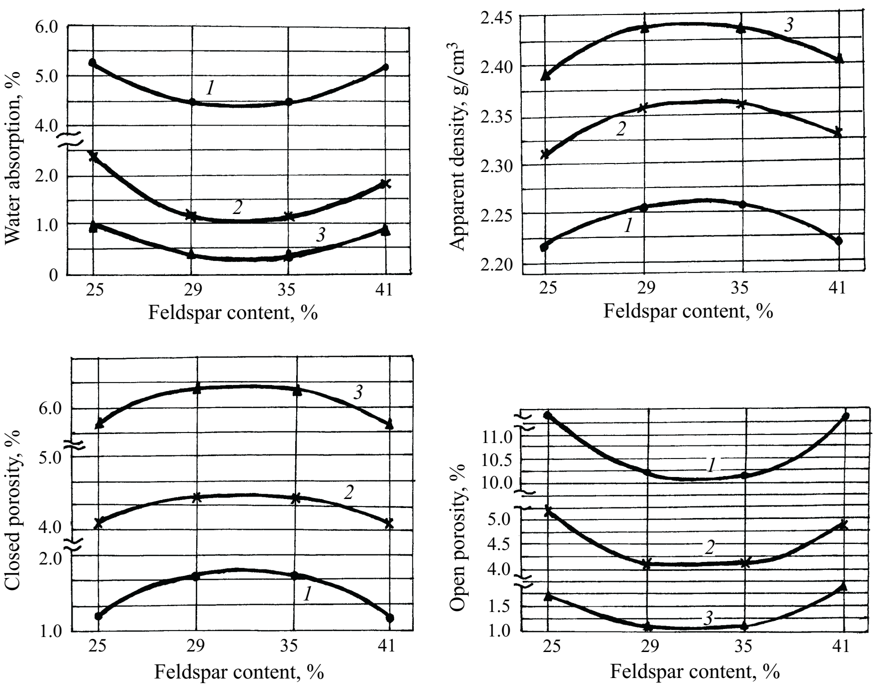

Fig. 2. Dependence of the sample properties on the feldspar content: *1*, *2*, and *3*) firing temperatures 1130, 1160, and 1190°C, respectively.

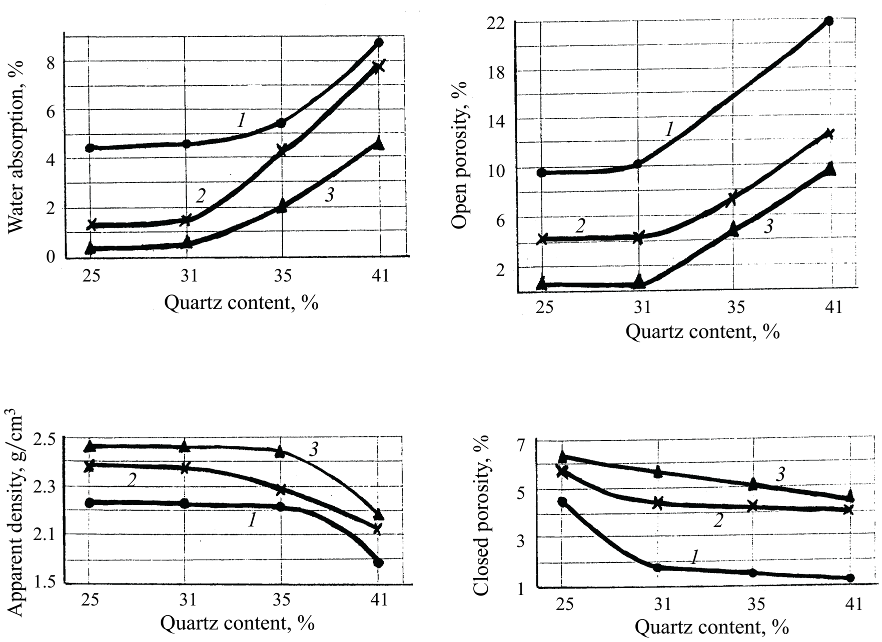

Fig. 3. Dependence of the sample properties on the quartz content. The same notation as in Fig. 2.

A distinguishing feature of the composition of granite mixtures for fast firing is an increased content of flux that allows a firing temperature of 1160 – 1200°C. The flux was pegmatite from the Chalm-Ozero deposit. The high $K_2O : Na_2O$ ratio in this pegmatite gives expectations of a decrease in the tendency for deformation in the experimental mixtures.

In designing experimental mixtures a phase diagram was used in which the variables were kaolinite, feldspar, and quartz, since the quality of the materials used makes it possible to calculate their rational composition. The region of the experimental compositions in the kaolinite – feldspar – quartz ternary system provides for formation of crock with a compact porcelain-like structure under the chosen conditions of synthesis (Fig. 1).

The experimental mixtures were prepared by the slip method in a ball mill (residue less than 0.8% on a No. 0063 sieve) with subsequent drying of the slip, crushing of the cakes, preparation of molding powder (moisture content 6%), molding of tiles (maximum molding pressure 25 MPa), drying of the intermediate product, and single-stage firing of it at a temperature of 1130 – 1230°C.

The effect of feldspar on the physicochemical properties of fired samples was determined from cross sections of the system with a constant content of quartz and a variable content of kaolinite and feldspar (Fig. 2). All curves exhibit clear extrema that correspond to a feldspar content in the experimental mixtures equal to 31 – 32%. With this content of feldspar, a maximum degree of sinterability, minimum values of water absorption, and maximum values of the fired sample density are achieved. With a higher alkali content, processes accompanied by gas emission and, as a rule, deformation of the articles (at increased firing temperatures) develop in the crock. The regularity noted is generally observed in system cross sections with different content (from 25 to 35%) and suggests the optimum feldspar content to be equal to 31%.

Optimization of the quartz content in the compositions considered was carried out by replacing kaolinite with quartz for the system cross section with the optimum feldspar content (Fig. 3).

It is known that the positive role of the quartz component in ceramic mixtures consists in increasing the resistance of articles to deforming stresses in heat treatment; however, an excessive quartz content increases the open porosity, decreases the mechanical strength of fired products, etc.

An optimum degree of product sintering is achieved with a quartz content close to 27%. An excess over this quantity of quartz in the ceramic mixtures degrades the physicochemical properties of the product.

TABLE 1

Firing tempera-ture, °C	Sample properties					
	water ab-sorption, %	apparent density, g/cm^3	porosity, %		fire shrinkage, %	deforma-tion, %
			open	closed		
1160	0.66	2.43	1.61	4.21	9.91	0.21
1175	0.31	2.56	0.94	4.35	9.95	0.37
1190	0.28	2.58	0.73	4.93	10.85	0.49
1200	0.42	2.51	0.82	5.20	10.51	0.73

Intense sintering of experimental mixtures without deterioration of their properties occurs in the temperature interval of 1160 – 1200°C. In order to refine the firing temperature for the optimized mixture composition, a series of firings was performed at different temperatures. The results obtained are shown in Table 1.

An improvement in the parameters of the articles is observed up to a maximum firing temperature of 1190°C, and on exceeding this temperature, the deformation is increased beyond the admissible limits, which is accompanied by signs of overburning.

An x-ray phase analysis established that the main crystalline phases in the fired products are mullite and quartz (Fig. 4), whose content, according to data of an electron microscope analysis, is as follows (%): 25 – 30 mullite, 15 – 20 quartz, 35 – 40 vitreous phase, 10 – 15 products of destruction of argillaceous material.

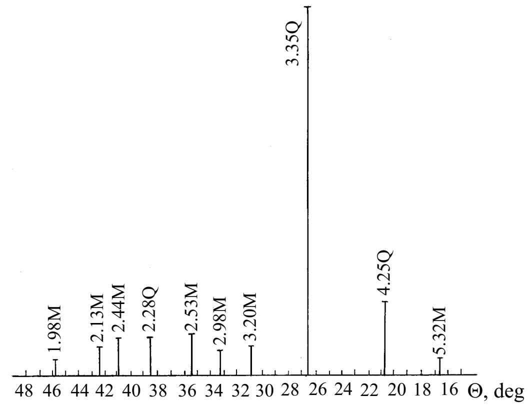

Fig. 4. X-ray pattern of the experimental sample: Q) quartz, M) mullite.

In the final stage of the study, the properties of an experimental mixture were compared to the properties of an industrial mixture used at the Keramin Company and produced under similar conditions. It was noted that with an approximately equal degree of sintering, the tendency for deformation is significantly lower in samples made of the developed mixture.

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